

Direct synthesis of dimethyl carbonate and propylene glycol using potassium bicarbonate as catalyst in supercritical CO₂

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The improved one-pot synthesis of dimethyl carbonate and propylene glycol from propylene oxide, supercritical carbon dioxide, and methanol with potassium bicarbonate as the catalyst has been reported in this paper. As far as we know, it is the first time to use potassium bicarbonate only as the catalyst in the production process which is simple and cheap. Satisfactory conversion rate of propylene oxide and yield of the products could be achieved at the optimized conditions with quite a small amount of by-products. Our new method offers an attractive choice for the production of dimethyl carbonate in large-scale industry efficiently and environmental friendly.

Keywords: direct synthesis, dimethyl carbonate, carbon dioxide, potassium bicarbonate, supercritical fluids.

INTRODUCTION

Because carbon dioxide (CO₂) is an abundant, inexpensive, and nontoxic biorenewable resource, it is an attractive raw material for incorporation into important industrial processes. CO₂ is also attractive as an environmentally friendly chemical reagent, and is especially useful as a phosgene substitute. Then the development of environmentally benign processes utilizing CO₂ has become a very attractive topic in recent years¹⁻³. The special properties of supercritical fluids (SCFs) give rise to a whole range of utilizations: reaction yields, rates, and selectivity can be adjusted by changing pressure; SCFs (especially CO₂) can be used as green solvents; mass transfer is improved for heterogeneous reactions due to the obviously increased solubility; and simultaneous reaction and separation may be achieved for some reactions^{2, 4}.

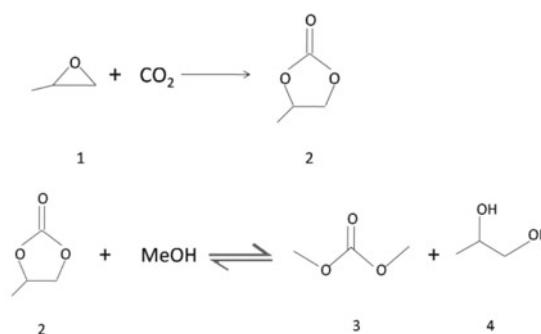
Synthesis of dimethyl carbonate (DMC) using CO₂ is one of the promising reactions for the purpose of the development of environmentally benign processes utilizing CO₂. DMC is a versatile compound that represents an attractive eco-friendly alternative to both methyl halides (or dimethyl sulfate) and phosgene for methylation and carbonylation processes, respectively. The application of DMC extends to polycarbonate synthesis, carbonylating reagents, polyurethane synthesis, alkylating reagents, octane boosters in gasoline, polar solvents, carbon-particle reducing agents for diesel engines, and so on⁵. Especially, DMC is gaining importance as a safe and environmentally benign alternative for phosgene in some kinds of reactions⁶.

Utilization of DMC in different applications is growing, so effective and clean synthesis routes are of great importance. Until now, there are two basic routes to synthesis DMC^{7, 8}. The first one is the methanolysis of phosgene with toxic gas which is harmful to the environment. Another way is the non-phosgene route which is based on the oxidative carbonylation of methanol. However, there are several obvious disadvantages of this route: safety and environmental concern due to the possible leakage of carbon monoxide; and the process being pricy

due to the noble metal catalyst. So the exploration of new clean ways for DMC synthesis is urgent.

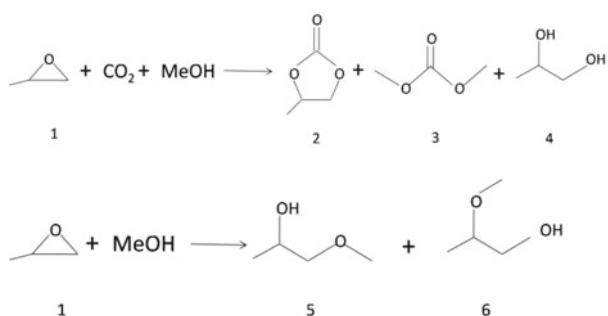
Direct synthesis routes of DMC from transesterification of cyclic carbonates is a new proposal to this problem which employs two original chemicals, CO₂ and methanol, with inorganic bases⁹, organometallic complexes¹⁰, and modified metallic oxide¹¹ as catalysts. The great advantage of this method is its facility. However, the conversion rate of this reaction is very low due to the thermodynamic limitations. The DMC can also be synthesized from CO₂ and ortho-esters¹² or acetals¹³. The disadvantage of this route is the high cost of the raw materials.

The two-step synthesis of DMC from epoxides, CO₂, and methanol is another effective non-phosgene method (Scheme 1) which produces a cyclic carbonate¹³⁻¹⁵. Different solid catalysts have been systematically studied for the two-step synthesis of DMC, and satisfactory results have been obtained. However, the major problems of this process are the decomposition of the catalyst and the hydrolysis of the carbonate.



Scheme 1. Two-step synthesis of DMC from epoxides, CO₂, and methanol

The one-pot reaction shown in Scheme 2 is a much facile process because it can eliminate the separation process after the first reaction step (Scheme 1). Unfortunately, this method is not successful because of the large amount of the by-products produced from the alcoholysis of epoxides (Scheme 2, second line)¹⁶⁻¹⁸. Therefore, the key to carry out the one-pot reaction is that the catalyst should be active for both the reactions



Scheme 2. One-pot reaction of DMC from epoxides, CO_2 , and methanol

in Scheme 1, while it should not be active to side reactions like alcoholysis of epoxides.

In this work, we investigate the direct one-pot synthesis of DMC from propylene oxide (PO), supercritical CO_2 (SC CO_2), and methanol with potassium bicarbonate (KHCO_3) as catalyst. The results indicate that inorganic salt KHCO_3 is an effective catalyst and it may also work as a dry agent to shift the equilibrium of the reaction in Scheme 1 (second line). High conversion rate of PO and yields of DMC and propylene glycol (PG) can be achieved. SC CO_2 acts as both the reactant and the solvent, and this process has special advantages. For example, compared with the two-step process, the separation process after the first reaction step is avoided; the reaction is conducted in homogenous supercritical conditions, where non-corrosive CO_2 is the main component in the reaction mixture, which prolongs the life of the catalysts. Compared with the previous result^[19] which employs potassium carbonate (K_2CO_3) as catalyst in the process, we can get the conclusion that the weak base is a better catalyst for the direct synthesis of DMC and PG.

EXPERIMENTAL SECTION

KHCO_3 , K_2CO_3 , magnesium oxide (MgO), N, N-dimethylformamide (DMF) and anhydrous methanol were produced by Beijing Chemical Reagent Factory (A. R. Grade). Propylene oxide was supplied by Shanghai Chemical Reagent Factory (A. R. Grade). CO_2 (>99.95%) was purchased from Beijing Analytical Instrument Factory. Methanol was dried with 4 Å molecular sieves. All the other chemicals were used without further purification.

The employed apparatus of synthesis DMC was shown in Figure 1. A stainless steel batch reactor (high-pressure cell) of 17.4 ml was used. The main components were a reactor, a constant temperature oil bath, a pressure gauge, a CO_2 pump, a magnetic stirrer, and a cold trap. The temperature fluctuation of the air bath was ± 0.5 K which was controlled by a PID temperature controller made by Beijing Tianchen Electronic Company (Model SX/A-1). The pressure gauge composed a pressure transducer (FOXBORO/ICT, model 93) and an indicator; its accuracy level was ± 0.05 MPa in the pressure range of 0–20 MPa.

In a typical experiment, the desired amount of catalyst, PO, and methanol were loaded into the reactor. Suitable amount of CO_2 was then charged into the reactor with a CO_2 sample bomb, and the amount of CO_2 charged was calculated from the weight difference of the sample

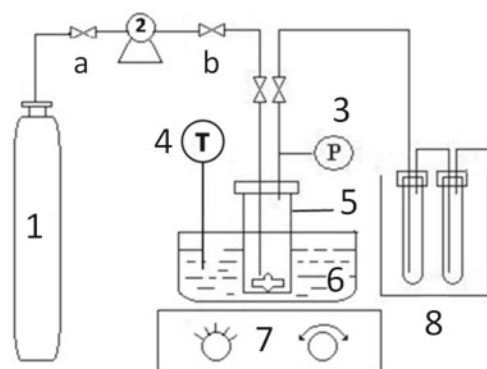


Figure 1. Schematic diagram of the apparatus for DMC synthesis. 1 – gas cylinder, 2 – high-pressure syringe pump, 3 – pressure gauge, 4 – temperature controller, 5 – reactor (high-pressure cell), 6 – oil bath, 7 – magnetic stirrer, 8 – cold trap, a, b – valves

bomb before and after charging. Then the reactor was placed into a temperature oil bath with a constant stir rate. After a certain time, the reactor was cooled down to 323.15 K, and then CO_2 was released slowly passing through the cold trap with DMF as an absorbent. The liquid chemicals in the reactor were extracted in situ by SC CO_2 at 12 MPa. Experiments showed that all the reactants and products were collected in the cold trap, and about 80 g of CO_2 was required to extract all liquid chemicals. Experiments proved that the amount of reactants and products entrained by CO_2 was negligible. The catalyst was left in the reactor, because it was not soluble in SC CO_2 . The liquid mixture in the reactor was analyzed by gas chromatography (Agilent 4890D, Agilent Technologies Inc.) with an Innowax capillary column (30 m \times 0.252 mm \times 0.25 μm) and a FID detector.

RESULTS AND DISCUSSION

In this work, we investigate the one-pot synthesis of DMC from PO, CO_2 , and methanol with KHCO_3 as catalyst. The DMC synthesis process actually includes three reactions as following: the first one is CO_2 reacts with PO to produce cyclic carbonate (propylene carbonate, PC); and the second one is the transesterification of methanol with PC to obtain DMC and PG. The third one is a side reaction which is the transesterification of methanol with PO with alcohol 5 (on Scheme 2) and 6 (on Scheme 2) as the products. The basic issue is how to obtain high conversions while avoiding thermodynamic restriction and the effect of reaction time is critically important.

According to the previous result about the direct synthesis of DMC and PG from PO, CO_2 , and methanol with potassium carbonate as catalyst¹⁹, we know that increasing the feed molar ratio of methanol to PO can improve the yield of DMC, but the percentage of the methanol reacted decreases with the ratio increasing. The yield in this work is defined as follows: Yield = (moles of product)/(moles of epoxides added). The conversion is defined as the ratio of the moles of the reactant reacted to the moles of the reactant taken initially. The 1:4:10 molar ratio of PO: CH_3OH : CO_2 is the best condition for the system under which the content of DMC in the liquid mixture after reaction is largest. Considering that the properties of K_2CO_3 and KHCO_3 are quiet similar,

the same molar ratio of the reactants is employed in this work. Figure 2 shows the dependence of the yield of DMC on the reaction time. It can be seen that the conversion of PO almost reaches 100% after 4 hours and the yield of DMC up to constant about 20%. It means that the reaction reaches equilibrium after about 4 h. In the following, the results with a reaction time of 4 hours are discussed without special indicated.

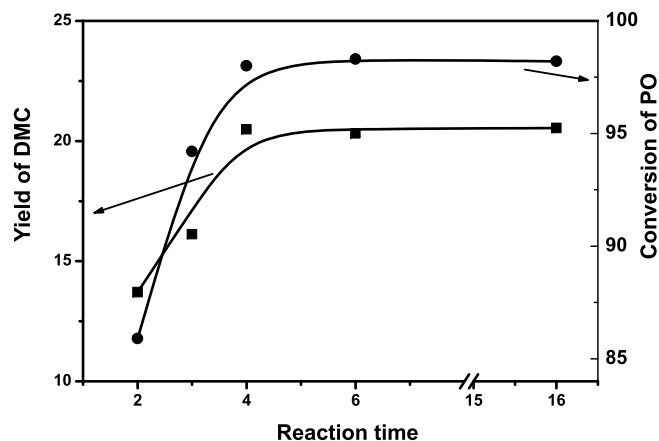


Figure 2. The PO conversion and DMC yield on reaction time. (The reaction condition: temperature 413.15 K, pressure 12 Mpa, the molar ratio of PO:CH₃OH:CO₂:K₂CO₃ = 1:4:10:0.065, the amount of PO in the reactor is 5 mmol.)

Up to now, the mature route to synthesize DMC using epoxides, CO₂ and methanol may be the Bhanage et al.¹⁷, who explored a two-step synthesis route using various basic metal oxide catalysts. They found that MgO was the best catalyst among the catalysts they used. They also carried out the direct synthesis using Mg contained catalysts, and they found that large amounts of by-products were produced, which were formed by methanolysis of epoxides^{14,17}. We also conduct the direct synthesis using this catalyst (MgO) under the reaction condition of this work, the yield of DMC is as low as 8.24% when PO is used as raw material, and a significant amount by-products is produced, which can be known from entry 1 in Table 1. Table 1 also shows the results of K₂CO₃ and KHCO₃ as catalyst with the 1:10:0.065 ratio of PO: CO₂:catalyst indicate that both of them are effective catalyst for the direct synthesis of DMC. The data in Table 1 indicates that the synthesis is a series of reactions involving a cyclic carbonate intermediate.

Molar ratio of methanol:PO is a critically important factor for the results as shown in Table 1, as well as the hydrolysis ability of catalyst. The side reaction at a lower ratio of methanol:PO with KHCO₃ as a relatively weaker base catalyst is under its unfavorable condition. In other words, with the 4:1 molar ratio of methanol:PO, the

side reaction of the transesterification of methanol with PO to the alcohol 5 and 6 (on Scheme 2) is not active. For example, the total yield of (5 + 6) is 11.94% and 10.16% for K₂CO₃ and KHCO₃ respectively. (Entry 2 and 3) However, increasing the molar ratio of methanol:PO activates the side reaction and then the total yield of alcohol (5 + 6) is increased obviously. For entry 3, 5, and 7, the total yield of alcohol (5 + 6) is 10.16%, 24.69% and 34.87% respectively with KHCO₃ as catalyst. The reason may be due to the over-alcoholysis of PO with too much methanol. In other words, compare K₂CO₃ with KHCO₃ as catalyst, we know that with a suitable ratio of methanol:PO, KHCO₃ will result in a slightly higher yield of DMC (Entry 2 and 3); while increasing the ratio of methanol:PO, higher yield of DMC can be obtained with K₂CO₃ which can prevent the over-alcoholysis of PC due to its higher hydrolysis ability.

CONCLUSIONS

In brief, the results indicate both K₂CO₃ and KHCO₃ are high efficient catalyst, while the yield of KHCO₃ is slightly higher. The conversion rate of PO is high while the yield of DMC can be up to 30%, and the amount of by-products (alcohol 5 and 6) is small which can be decreased to 10% of the final products. SC CO₂ acts as both reactant and solvent. This route may play an important role in the large-scale production of DMC due to its great advantages, for example, it is facile, the raw materials are cheap, and the amount of the by-products is small.

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Table 1. The DMC synthesis results with different catalysts*

Entry	Catalyst	MeOH:PO [molar ratio]	PO Conv [%]	Yield [%]			
				DMC	PC	PG	5 + 6
1	MgO	4:1	89.23	8.24	32.5	10.21	40.26
2	K ₂ CO ₃	4:1	98.27	20.31	33.84	34.20	11.94
3	KHCO ₃	4:1	99.53	23.10	35.46	32.06	10.16
4	K ₂ CO ₃	10:1	98.00	30.48	22.09	25.58	23.94
5	KHCO ₃	10:1	96.87	16.84	32.17	27.22	24.69
6	K ₂ CO ₃	15:1	98.39	19.55	30.11	21.87	29.07
7	KHCO ₃	15:1	97.41	16.29	25.15	22.95	34.87

* The reaction condition: temperature 413.15 K, the molar ratio of PO: CO₂: catalyst = 1:10:0.065, the amount of PO in the reactor is 5 mmol.

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